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The change of the structural and thermodynamic properties of water from ambient to supercritical conditions as seen by computer simulations

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Abstract. Results of Monte Carlo simulations with various polarizable potential models and reverse Monte Carlo simulations of water are reported at different thermodynamic state points from ambient to supercritical conditions. It is shown that polarizable potential models can reproduce the change of the experimental partial pair correlation functions of water with the temperature and density considerably better than simple nonpolarizable models. Thus, for instance, only the polarizable models can reproduce the experimentally observed elongation of the hydrogen bonds with increasing temperature and decreasing density. On the other hand, the densities of the polarizable water models decrease unexpectedly fast with increasing temperature, which affects also the reproduction of other thermodynamic properties at states of high pressure and high temperature. In analysing the properties of the hydrogen bonded clusters it is found that the space-filling percolating network of the molecules breaks down around the critical point, although a large number of hydrogen bonds still remain in the system above the critical point.

1. Introduction

The intensive investigation of the structure of water around the critical point has only started in this decade. The $g_{ij}(r)$ partial pair correlation functions of supercritical water were first measured in 1993 using the neutron diffraction with isotopic substitution (NDIS) method [1]. The obtained data deviated strongly from the results of the early computer simulations [2–4]. Computer simulations were unable to reproduce the experimentally observed elongation of the hydrogen bonds when approaching the critical point, and also resulted in a considerably smaller first $g_{OO}(r)$ and larger $g_{OH}(r)$ peak than the experimental data. These deviations stimulated further experimental as well as computer simulation studies of high pressure high temperature water. Firstly, following some criticisms of the quality of the original experimental data [5, 6] the NDIS experiments were repeated with several improvements introduced both in the experimental setup and in the data reduction procedure [7]. The results of these new measurements were consistent with the picture obtained from several other kind of experiment [8] as well as with the results of an *ab initio* molecular dynamics simulation [9]. Secondly,

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several new, polarizable water models were developed [10–12] in order to take the change of the dipole moment of the water molecules with the thermodynamic conditions into account in the simulations. The resulting $g_{ij}(r)$ showed considerably better agreement with the new experimental data than those of the simple nonpolarizable models [10–14]. Moreover, the new experimental $g_{ij}(r)$ were successfully reproduced by reverse Monte Carlo (RMC) modelling, and thus configurations fully consistent with the results of these experiments have been generated [13, 15]. The fact that the $g_{ij}(r)$ obtained from RMC simulations or conventional simulations with polarizable water models do not contradict the results of the NDIS experiments allows us to study the change of the molecular level structure of water meaningfully on the basis of these computer simulations.

Besides the structural analysis the investigation of the thermodynamic properties of the new polarizable models is also of great interest. Simple nonpolarizable models, such as SPC/E [16] or TIP4P [17], account for the induced dipole moment of the molecules in an average way, using charge distributions which correspond to considerably larger molecular dipole moment than the gas phase value of 1.85 D. However, in this way the change of the dipole moment with the temperature and density cannot be accounted for. On the other hand, polarizable models take the induction effect of the electric field of the surrounding molecules explicitly into account, and thus it is sensible to assume that besides the structure these models can also provide a better description of the thermodynamical properties of water than simple nonpolarizable ones.

This paper focuses on the change of both structural and thermodynamic properties of water from ambient conditions up to the critical point. Structural properties are analysed on configurations which are as consistent with the experimental data as possible. Such configurations were generated by RMC simulations [13, 15]. Besides the $g_{ij}(r)$ we focus here on the change of the hydrogen bonded clusters. The most important thermodynamic properties of several polarizable and nonpolarizable water models are also presented, and possibilities of improving these models are discussed.

2. Calculation details

The details of the performed simulations are given elsewhere [13, 14], so only a brief description is presented here. In the RMC simulations [13] the intermolecular part of the three $g_{ij}(r)$ obtained from the NDIS experiment of Soper *et al* [7] were simultaneously fitted. In each simulation 512 rigid molecules were placed into a cubic simulation box, which was surrounded by periodic images of itself in the usual way. The edge length of the simulation boxes were fixed in accordance with the experimental density of the given state point. The closest allowed approaches of the O–O, O–H and H–H atom pairs were set to 2.4, 1.5 and 1.7 Å, respectively. Moves violating these constraints were rejected without any further testing.

Conventional Monte Carlo (MC) simulations of 256 molecules were also performed both on the (N, V, T) and the (N, p, T) ensemble with three polarizable water models, namely the Brodholt–Sampoli–Vallauri (BSV) [10], the Chialvo–Cummings (CC) [11] and the Dang–Chang (DC) [12] ones. For comparison, simulations with the nonpolarizable TIP4P and SPC/E models were also carried out. A cubic simulation box and standard periodic boundary conditions were used. All interactions of molecules with O–O separation larger than 9 Å were truncated to zero. The long range part of the electrostatic interactions were taken into account by the reaction field correction method [18], whereas that of the Lennard-Jones interactions with the assumption that $g_{OO}(r) \equiv 1$ beyond 9 Å. The exact formulae of the calculation of the energy of the system and the dipole moment of the molecules are given elsewhere [14, 19].

3. Structural results

3.1. Partial pair correlation functions

Figure 1 shows the comparison of the $g_{OO}(r)$ and $g_{OH}(r)$ functions as obtained from the NDIS experiment of Soper *et al* [7] with the results of RMC simulations as well as with MC simulations on the (N, V, T) ensemble using the polarizable BSV and the nonpolarizable TIP4P models at three different state points. As is evident, the RMC simulation reproduced the experimental data very accurately in each case. The only small deviation is at the first peak of $g_{OH}(r)$ at 573 K, which is slightly underestimated by RMC.

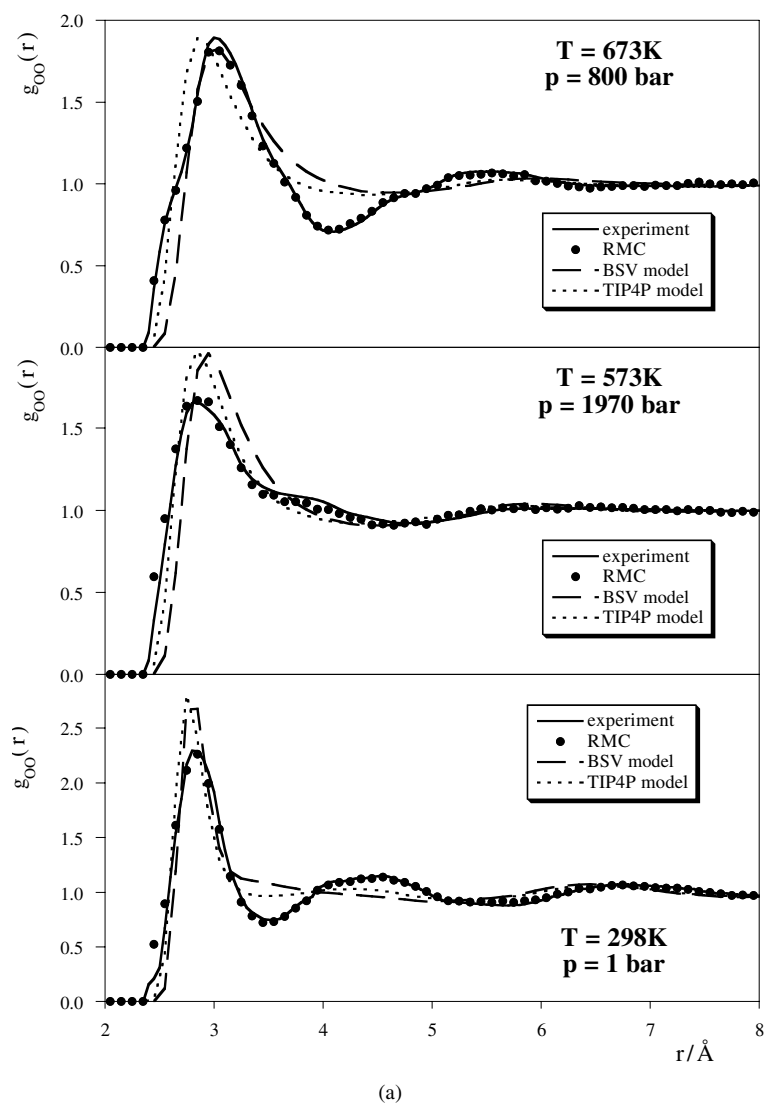


Figure 1. Comparison of (a) the $g_{OO}(r)$ and (b) the $g_{OH}(r)$ functions as obtained from NDIS experiment [7], RMC simulation and (N, p, T) Monte Carlo simulations using the polarizable BSV and the nonpolarizable TIP4P models.

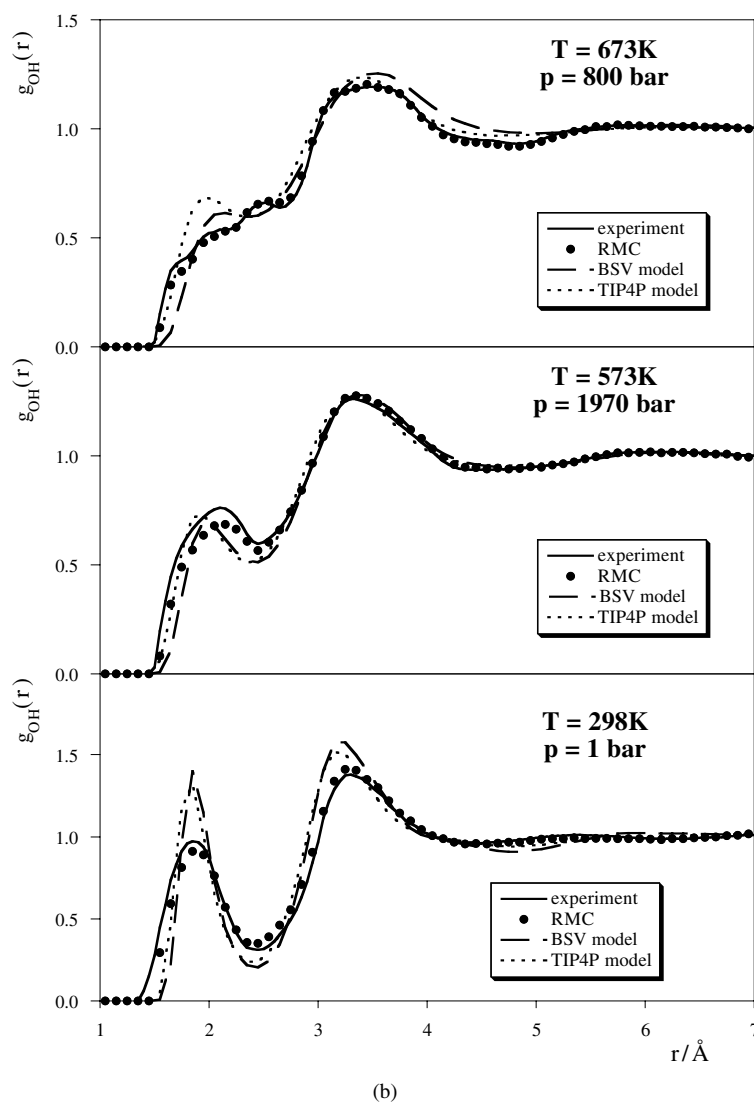


Figure 1. (Continued)

The first peak of the experimental $g_{OO}(r)$ function is sufficiently well reproduced in every case by both models, although they slightly overestimate its height below the critical point. The position of this peak is clearly better reproduced by the BSV than the TIP4P model. Both models reproduce the experimental $g_{OO}(r)$ rather poorly around its first minimum, between 3 and 5 Å, at all the three state points. When comparing the $g_{OH}(r)$ functions the two potential models behave in a markedly different way. Namely, the position of the first peak of $g_{OH}(r)$ always appears at about 1.9 Å with the TIP4P model, independently from the thermodynamic conditions. However, this peak of the BSV model shifts towards larger r values with increasing temperature and decreasing density, and thus, in contrast to TIP4P, this model is able to reproduce the experimentally observed elongation of the hydrogen bonds when approaching the critical point. Moreover, the change of the height of this peak with

the thermodynamic conditions, monitoring the change of the number of existing hydrogen bonds in the system, is also far better reproduced by the polarizable BSV model than by TIP4P. It should also be emphasized that the studied three polarizable as well as the two nonpolarizable models resulted in rather similar $g_{ij}(r)$ at all the three thermodynamic states. Thus, the above discussed differences in the structure of BSV and TIP4P water demonstrate the improvement in describing the structure of water in a wide range of thermodynamic states when the polarizability of the molecules is explicitly included in the model.

3.2. Hydrogen bonded clusters

The size distributions of the hydrogen bonded water clusters are shown in figure 2 as obtained from the RMC simulations at three different thermodynamic state points. Two molecules

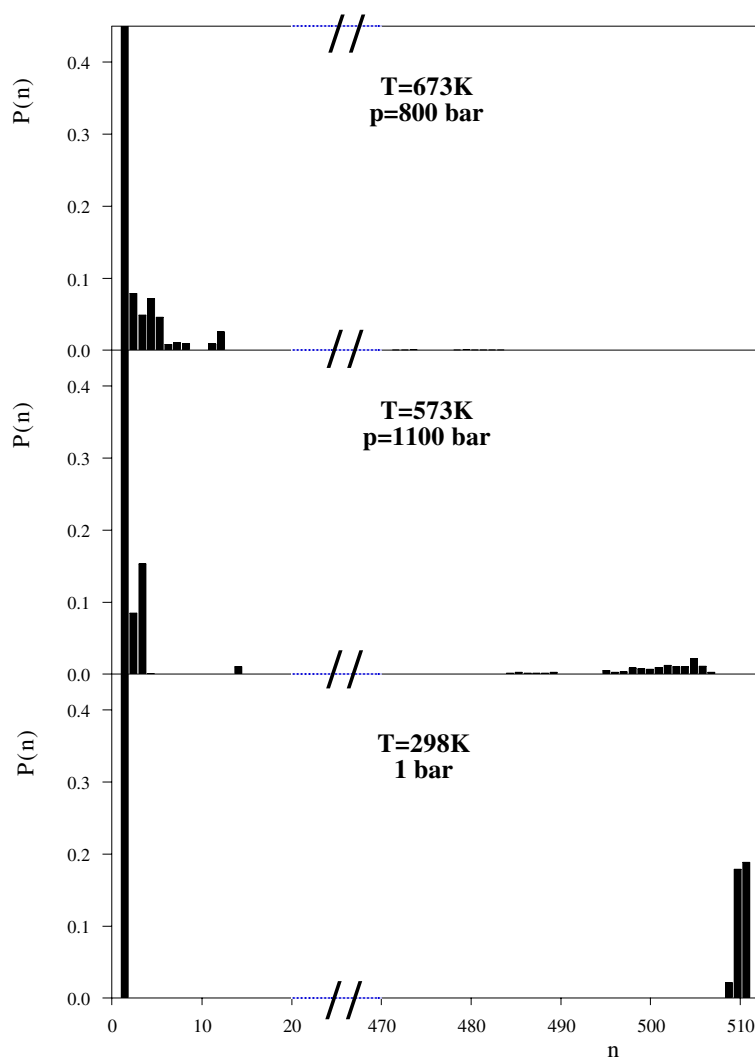


Figure 2. Size distribution of the hydrogen bonded water clusters at three different thermodynamic state points as obtained from the RMC simulations.

are considered to be hydrogen bonded if their O–O and shortest O–H separations are both smaller than the first minimum distance of the corresponding $g_{ij}(r)$ [13]. As is evident, at ambient conditions the molecules are forming a space-filling percolating hydrogen bonding network. It is found that, with the exception of 1.57 unbounded water molecules on average, all the molecules belong to the same cluster at this state point. Clusters built up by about 500 molecules are present even at 573 K and 1100 bar, indicating that the space-filling hydrogen bonding network of the molecules still exists here. However, at the supercritical state of 673 K and 800 bar these clusters have disappeared, and the percolating network of the molecules is broken up to small hydrogen bonded oligomers. The average cluster size is only 18.15, and on average 18.5 molecules out of the 512 have no hydrogen bonded neighbours at all. However, in spite of the breakdown of the percolating network there is still a large number of intact hydrogen bonds present in the system at this thermodynamic state point. The molecules are still participating in 2.9 hydrogen bonds on average, and 12.8% of them have more than four hydrogen bonded neighbours.

4. Thermodynamic results

The most important thermodynamic results obtained on both the (N, V, T) and the (N, p, T) ensemble at three different state points with the polarizable BSV and CC and the nonpolarizable SPC/E models are compared with experimental data in table 1. The table also includes the dielectric constants ϵ , which were calculated by the molecular Ornstein–Zernike theory [21], using a self-consistent mean field approach [22] for the polarizable models. Due to the approximations of these methods the resulting ϵ values are 10–15% lower than simulation results. Details of these calculations are given elsewhere [14, 23].

Table 1 shows that, in contrast to the $g_{ij}(r)$, the temperature dependence of the thermodynamic properties of water are far better reproduced by the SPC/E than by any of the

Table 1. Thermodynamic properties of different water models as obtained from MC simulations at three different thermodynamic state points. Experimental data are given for comparisons. State points I, II and III correspond to $\{T = 298 \text{ K}, p = 1 \text{ bar}\}$, $\{T = 573 \text{ K}, p = 1970 \text{ bar}\}$ and $\{T = 673 \text{ K}, p = 800 \text{ bar}\}$, respectively.

Model	State point	(N, V, T)		(N, p, T)		
		U (kJ mol ⁻¹)	ϵ^a	H (kJ mol ⁻¹)	ρ_m (Å ⁻³)	ϵ^a
BSV	I	-41.7	132.2	-42.7	0.0362	173.2
	II	-27.8	26.7	-22.3	0.0278	23.4
	III	-19.9	11.7	-13.3	0.0165	7.8
CC	I	-40.3	104.8	-39.4	0.0296	78.6
	II	-26.4	24.9	-17.4	0.0230	16.1
	III	-19.2	11.5	-8.2	0.0121	5.1
SPC/E	I	-41.7 ^b	59.6	-42.3 ^b	0.0352	63.7
	II	-28.2 ^b	22.5	-24.8 ^b	0.0296	22.5
	III	-22.9 ^b	12.8	-21.3 ^b	0.0214	12.6
Experiment ^c	I	-41.5	78.6	-41.5	0.0334	78.6
	II	-30.1	27.9	-26.0	0.0296	27.9
	III	-23.1	14.5	-20.9	0.0217	14.5

^a The dielectric constants of the models are calculated from the molecular Ornstein–Zernike theory.

^b The 5.22 kJ mol⁻¹ energy needed to increase the dipole moment from 1.85 to 2.35 D is included.

^c Results obtained from the Saul–Wagner equation of state [20] are shown as ‘experimental’ with the exception of the dielectric constants, for which results of the equation of state published in [24] are shown.

two polarizable models in this range of thermodynamic states. The results of the DC and TIP4P models are similar to the results of the BSV or CC and the SPC/E models, respectively [14, 23]. At ambient conditions all the models reproduce the internal energy U and enthalpy H of the system within 3%. However, with increasing temperature and pressure the magnitude of these quantities decrease much faster for the polarizable models than the experimental data. Thus, at 673 K and 800 bar the internal energies of the BSV and CC models are about 15% smaller from the (N, V, T) simulation than the experimental value. In addition, when simulations are performed on the (N, p, T) ensemble the molecular number density ρ_m of these systems also found to decrease much faster with increasing temperature than the experimental data (at 673 K and 800 bar the density of the BSV and CC water is only about 75% and 55% of that of real water). This results in an additional decrease of the enthalpy of these systems. In contrast to the 15% difference of the U values on the (N, V, T) ensemble, the H value of the BSV and CC models are 35% and 60% smaller in magnitude than the experimental values at the 673 K state point. The unexpectedly fast decrease of the density of these systems reflects also in the difference of the ε values as obtained on the two ensembles. The too sharp decrease of ρ_m with increasing T was also observed in a much more limited temperature range, between 268 and 328 K, for the BSV model, which reproduced the temperature of the experimental density maximum at 277 K excellently; however, it resulted in about five times larger $\Delta\rho/\Delta T$ values than the experimental data [19]. In contrast to the polarizable models, SPC/E reproduces the experimental U , H and ρ_m values within 5–6% at all the three state points. Also its ε values obtained on the two ensembles agree within 5–6% in all cases.

One of the reasons for this failure of the polarizable models in reproducing the change of the density with the temperature and pressure can be that these models were solely parametrized to the properties of ambient water. Since the thermodynamic properties of these models are much more sensitive to the small changes of their parameters than the $g_{ij}(r)$, a careful re-parametrization of any of them could improve the thermodynamic results without deteriorating the reproduction of the $g_{ij}(r)$. A more fundamental improvement would involve the change of the functional form of these models. Since the steepness of the potential function is directly related to the pressure, and hence on the (N, p, T) ensemble to the density of the system, its appropriate modification at short distances (either by employing exp-6 type rather than Lennard-Jones interaction or by applying appropriate damping of the polarization energy at short intermolecular separations) would probably help to overcome this problem.

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